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The generalized active space concept for the relativistic treatment of electron correlation. II. Large-scale configuration interaction implementation based on relativistic 2- and 4-spinors and its application

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The extension of a relativistic double group configuration interaction (CI) formalism to the use of 2- and 4-spinors is presented. We first elucidate the theoretical aspects of the formalism that is needed to work with spinors that are optimized with a Hartree–Fock scheme that includes spin–orbit coupling. We then describe a new general implementation for the computation of sigma vectors and n-particle density matrices that occur in direct CI algorithms. Sample calculations of the spin–orbit splitting in atoms with one particle or hole in an otherwise closed shell configuration ℓ^1 ($\ell=1,2,3$) and molecules containing such atoms illustrate the advantage of treating this effect in a basis of true spinors rather than in a basis of scalar relativistic orbitals as is conventionally done.
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I. INTRODUCTION

The simultaneous description of electron correlation and relativistic effects in atomic and molecular electronic structure calculations of heavy elements is desirable in general (like in Lanthanide and Actinide compounds[1]) and a requirement in many cases (e.g., in the heavy p block elements[2]) when spectroscopic data of high precision are aimed at. The resulting need to correlate many electrons suggests the use of size-extensive coupled cluster approaches, but these are usually incapable of describing low spin open-shell cases and/or static electron correlation. For these reasons, configuration interaction (CI) approaches are still worth pursuing.

A number of programs for performing relativistic CI calculations has been reported, e.g., the DIRRCI code in the DIRAC package,[3] the COLUMBUS CI program[4] using effective core potentials, or a newly developed spin–orbit CI code[5,6] based on a multireference CI approach (others are mentioned in Refs. 7 and 8).

State of the art in large-scale CI calculations was, however, so far to use orbitals that are obtained without consideration of spin–orbit coupling. These so-called scalar relativistic molecular orbitals (SRMOs) are readily obtained by modern quantum chemistry program packages (e.g., MOLCAS[9]) that include scalar relativistic corrections via an effective core potential or a variationally stable Hamiltonian (e.g., the Douglas–Kroll–Hess Hamiltonian). A disadvantage of this approach shows up if one considers states for which spin–orbit coupling significantly alters the wave function. An accurate description of such a state with a CI expansion based on SRMOs requires extremely long expansion lengths as the CI expansion should not only take care of electron correlation corrections but also serve to include the orbital relaxation induced by spin–orbit coupling. More compact and accurate representations of the wave functions, especially in the heavy main group atoms and their molecular compounds[2] are possible by an expansion based on relativistic 4- (or approximate 2-) molecular *spinors* (RMSs). A complication is that such spinors transform according to double group symmetry representations necessitating modification of the algorithms that are used to solve the (direct) CI equations. Still, we think that CI calculations based upon spinors may well become more efficient than the traditional approach since much shorter expansions may be used.

A preceding publication[10] has at length dealt with a new configuration interaction (CI) implementation for relativistic quantum chemistry applications. The key concept is the introduction of generalized active spaces (GAS) which allow for an arbitrary division of orbital/spinor spaces and, therefore, a very flexible definition of trial wave functions. For not too large systems, for which the size extensivity defects of CI are not so important, one can then account for both dynamical and static electron correlation while simultaneously including spin–orbit coupling effects. An efficient implementation, like the LUCI-type algorithms developed by one of us, allows for near full CI accuracy by using very long expansions. These key points also comprise the improvements over the aforementioned DIRRCI program which is also

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based on molecular spinors, but limited to restricted active space (RAS) type expansions and, furthermore, to expansions of not more than a few million determinants.

In the current paper we discuss the construction of a new interface that couples the CI program to the general relativistic quantum chemistry program DIRAC[3] that provides for the spinor optimization at the Hartree–Fock level. We plan to report a more extensive interface to the molecular MCSCF implementation in DIRAC in the near future. The optimization of the CI-wave function using a direct CI algorithm is discussed in detail and we show that the main task in the direct CI algorithm, the computation of the sigma vectors, can be carried out by a general algorithm that is also suited for the computation of density matrices. This will greatly simplify the work on relativistic multiconfiguration self-consistent field (MCSCF) wave functions.

All implementations could be realized by generalizing a newly developed set[11] of efficient routines from the LUCIA code.[12] These routines were originally created for the computation of nonrelativistic sigma vectors over general n-particle operators or n-particle density matrices as required in the Hilbert-space coupled-cluster (CC) formalism. The excitation class formalism that was developed turned out to be very useful for our present purpose as well.

The application section starts with a study of the ground-state spin–orbit splitting in three atoms with significantly differing radial expectation value of the ground-state spinor components (Tm, Lu, and Tl). Since the strength of the spin–orbit splitting varies strongly with the angular momentum of the open shell we can then compare the effect of using a spinor instead of a spin–orbital basis in both the strong (Tl) and weak (Tm) limit. Next we will consider application to the ClO molecule for which both experimental data and accurate coupled-cluster single double (triple) [CCSD(T)] reference values are available.

The paper is structured as follows: The theory section commences with important aspects of the transition from SRMOs to RMSs. We further discuss the excitation class formalism for structuring the CI wave function, the interface of the CI program to the DIRAC package, and finally the efficient computation of CI sigma vectors and density matrices in the excitation class formalism in detail. The next section of the paper reports atomic and molecular applications of the new code in direct comparison with other existing approaches. We finally draw conclusions for future work in the light of the acquired results.

II. THEORY AND IMPLEMENTATION

This section covers the new development work and strongly refers to the theoretical formalism from Ref. 10 to avoid repetition. We assume that spinors are obtained using a Kramers-restricted algorithm[13] and that all spinors transform according to a double group irreducible representation. All spinors are related to a Kramers partner and we label these so-called Kramers pairs by lowercase indices i, j, k, and l. The individual partners are distinguished by either placing or not placing a bar over this index.

The computation of a sigma vector from a given trial vector and that of a (transition) density matrix from two vectors can be cast in almost the same structure. To illustrate the construction of a sigma vector we consider the expression of the relativistic two-particle Hamiltonian in a basis of Kramers spinors[10,14,15]

$$\hat{H}^{2-el}=\tfrac{1}{2}\sum_{ijkl}\left[(ij|kl)x^{++}_{ijkl}+(\overline{ij}|kl)x^{+\,+}_{\overline{ij}kl}+(\mathbf{\overline{ij}|kl})\mathbf{x}^{+\,+}_{\mathbf{\overline{ij}kl}}\right]$$
$$+\tfrac{1}{4}\sum_{ijkl}(\overline{ij}|\overline{kl})x^{+\,+}_{\overline{ij}\overline{kl}}+\tfrac{1}{8}\sum_{ijkl}\left[(\overline{ij}|\overline{kl})x^{+\,+}_{\overline{ij}\overline{kl}}\right.$$
$$\left.+(i\overline{j}|k\overline{l})x^{+\,+}_{i\overline{j}k\overline{l}}\right]\},\qquad(1)$$

and take a single term (given in boldface) consisting of a Kramers replacement operator

$$x^{+\,+}_{\overline{ij}kl}=-a^\dagger_i a^\dagger_k a^-_j a_l-a^\dagger_i a^\dagger_l a^-_j a^-_k+a^\dagger_j a^\dagger_k a^-_i a_l+a^\dagger_j a^\dagger_l a^-_i a^-_k,$$

derived from the generic formula for double replacement operators in Ref. 10 and an integral $(\overline{ij}|kl)$. Considering only the first creator-annihilator string, the term becomes

$$\sum_{ijkl}(\overline{ij}|kl)a^\dagger_i a^\dagger_k a_l a^-_j.\qquad(2)$$

The corresponding contribution to the sigma vector appears as

$$\sigma^{+1}(\mathcal{T},\mathcal{T}^\dagger)=\sum_{ijkl}\sum_{\mathcal{S},\overline{\mathcal{S}}}(\overline{ij}|kl)A^{\overline{\mathcal{T}},\overline{\mathcal{S}}\,\overline{\mathcal{S}}}_{\overline{ij}kl}C_{\mathcal{S},\overline{\mathcal{S}}},\qquad(3)$$

where $A^{\overline{\mathcal{T}},\overline{\mathcal{S}}\,\overline{\mathcal{S}}}_{\overline{ij}kl}=\langle\mathcal{T}^\dagger\overline{\mathcal{T}}^\dagger|a^\dagger_i a^\dagger_k a_l a^-_j|\mathcal{S}^\dagger\overline{\mathcal{S}}^\dagger\rangle$ is the coupling coefficient with $|\mathcal{S}^\dagger\overline{\mathcal{S}}^\dagger\rangle$ the Slater determinant defined by strings of spinor creation operators $\mathcal{S}^\dagger$ and $\overline{\mathcal{S}}^\dagger$, and $C_{\mathcal{S},\overline{\mathcal{S}}}$ is the expansion coefficient referring to this determinant in the CI expansion of the wave function.

The real part of the 2-particle density matrix fragment takes the form

$$\rho^r(2)(\overline{ij}kl)=\sum_{\mathcal{S},\overline{\mathcal{S}}}\sum_{\mathcal{T},\overline{\mathcal{T}}}C_{\mathcal{T},\overline{\mathcal{T}}}A^{\overline{\mathcal{T}},\overline{\mathcal{S}}\,\overline{\mathcal{S}}}_{\overline{ij}kl}C_{\mathcal{S},\overline{\mathcal{S}}},\qquad(4)$$

and comparing Eqs. (3) and (4) we see that by a proper ordering of the summation loops the contractions only differ in the specification of the multiplicative factors $(\overline{ij}|kl)$ and $C_{\mathcal{T},\overline{\mathcal{T}}}$, respectively. This makes the computation of the sigma vector very similar to that of the density matrix and enables us to use the same program code for both tasks.

The initial version of the LUCIAREL code as presented in Ref. 10 had to be extended to include sigma vector contributions that involve a change of the Kramers projection quantum number in the 2-particle operator. This contribution is zero in an orbital basis but has to be accounted for in a spinor basis as is easily shown by the following argument. Let i be an unbarred spinor and $\overline{j}$ a barred spinor with contributions of both α and β spin functions. Then a density $\langle i|\overline{j}\rangle$ of a two-electron integral $(i\overline{j}|kl)$, e.g., is nonvanishing due to nonzero spin integrations

$$\langle i(\alpha)+i(\beta)|\overline{j}(\alpha)+\overline{j}(\beta)\rangle=\langle i(\alpha)|\overline{j}(\alpha)\rangle+\langle i(\beta)|\overline{j}(\beta)\rangle$$
$$\neq 0,$$

no matter what type of operator is involved if true *spinors* are used. If *spinorbitals* (i.e., two-spinors for which only one of the components is nonzero) are chosen it is either the integral itself or the coupling coefficient that vanishes. This assumption, made in the older implementation, is now invalid. Straightforward extension of the formalism described in Ref. 10 would, therefore, call for implementation of additional sigma vector routines that consider this *Kramers flip* in the 2-electron operator explicitly. Instead of programming this addition we, however, chose to take another route and convert the algorithms to the excitation class formalism. In this formalism the detailed sigma and density computation is controlled at a higher level when the partitioning of the Hamiltonian is defined, and this makes the implementation of additional terms much simpler, as we will discuss below.

TABLE I. Excitation class ordered operators in second quantization and corresponding integrals.

Operator	Integral class	Kramers flip type
$a_i^\dagger a_j$	h_{ij}	$\Delta M_k=0$
$a_{\bar{i}}^\dagger a_{\bar{j}}$	$h_{\bar{i}\bar{j}}$	$\Delta M_k=0$
$a_i^\dagger a_k^\dagger a_l a_j$	$(ij\|kl)$	$\Delta M_k=0$
$a_{\bar{i}}^\dagger a_k^\dagger a_l a_{\bar{j}}$	$(i\bar{j}\|k\bar{l})$	$\Delta M_k=0$
$a_i^\dagger a_{\bar{k}}^\dagger a_l a_{\bar{j}}$	$(\bar{i}j\|\bar{k}l)$	$\Delta M_k=0$
$a_i^\dagger a_{\bar{j}}$	$h_{i\bar{j}}$	$\Delta M_k=+1$
$a_{\bar{i}}^\dagger a_j$	$h_{\bar{i}j}$	$\Delta M_k=-1$
$a_i^\dagger a_k^\dagger a_l a_{\bar{j}}$	$(ij\|k\bar{l})$	$\Delta M_k=+1$
$a_i^\dagger a_{\bar{k}}^\dagger a_l a_j$	$(i\bar{j}\|\bar{k}l)$	$\Delta M_k=-1$
$a_i^\dagger a_k^\dagger a_l a_{\bar{j}}$	$(ij\|\bar{k}\bar{l})$	$\Delta M_k=+2$
$a_{\bar{i}}^\dagger a_{\bar{k}}^\dagger a_l a_j$	$(\bar{i}\bar{j}\|\bar{k}l)$	$\Delta M_k=-2$

A. Excitation class formalism

The Hamiltonian (or in general any operator) can be defined by its total symmetry, a type label which gives the maximum number of particles involved, and the different classes of excitation operators that appear. To divide the excitation operations into different classes we consider the number of ''Kramers flips'' that they induce. These Kramers flips are equivalent to spin-flips in nonrelativistic formalisms and replace a barred spinor by an unbarred spinor or vice versa. As a particular excitation operator will always refer to a specific integral [cf. Eq. (2)] we can then also use the chosen excitation class ordering to determine the ordering of all involved integrals. Following this scheme Hamiltonians may now be distinguished in a number of types, depending on the level of sophistication that is used in the description of spin–orbit coupling:

	Excitation classes	
Type	1-particle terms	2-particle terms
1	$\Delta M_k=0$	$\Delta M_k=0$
2	$\Delta M_k=0,\pm 1$	$\Delta M_k=0$
3	$\Delta M_k=0,\pm 1$	$\Delta M_k=0,\pm 1,\pm 2$
4	like 3, spinor basis, integrals with an even number of bars	
5	like 3, spinor basis, integrals with an arbitrary number of bars	

A nonrelativistic Hamiltonian that does not include spin–orbit coupling operators corresponds to type 1, whereas a Hamiltonian in which spin–orbit coupling is described by a mean-field spin–orbit operator has only one-particle Kramers-flip operators and corresponds to type 2. For SRMOs, only types 1–3 will occur. When spinors form the basis, type 4 is relevant and, in case of low or no applicable point group symmetry (see Sec. II B 1), type 5 may also be relevant. A special case of a Hamiltonian containing type 2 operators occurs in a mean-field spin–orbit method that is based on the spinfree DIRAC formalism.[16] Here spin–orbit integrals are formed using a molecular mean-field expression. This method is currently being implemented by two of us (T.F. and L.V.).

The ordering of the classes is hardwired in the program as shown in Table I. With this classification we can subdivide the Hamiltonian in terms of the active excitation classes. The routines that perform the actual contractions only need to know which classes are active which means that the information corresponding to the Hamiltonian itself is only used in the higher levels of the code. We, therefore, made the routines performing the actual sigma and density evaluation entirely general and independent of the particular Hamiltonian that is defined. Incorporation of new Hamiltonians is now trivial since it merely requires adding the appropriate information in the setup routine. Furthermore, because the set of integrals contained in the operators is completely defined by the strings that are used in the actual calculation, one may easily discard integrals which are not required in a particular CI in the sorting step. This makes it easy to run multiple CI calculations using one set of molecular integrals and eliminates costly additional index transformations.

B. Integral interface to the DIRAC formalism

The earlier version of LUCIAREL assumes that each spinorbital can be decomposed into a spatial part, transforming according to a specific boson irrep, and a spin part. With spinors such a decomposition is impossible as each spinor will be built from functions that belong to different boson irreps. In the new implementation we, therefore, removed all reference to spatial symmetry and only consider the compound fermion irrep of the spinor in the appropriate double group. In the interface to DIRAC, where symmetry handling is limited to D_{2h}^* and its subgroups, this fermion irrep is simply the parity. It then suffices to label each spinor as either unbarred or barred and (in case of inversion symmetry) as *gerade* or *ungerade*. The CI code follows this designation.

1. Double group symmetry

The subgroups of D_{2h}^* can be divided into so-called real, complex, and quaternion groups.[13] The difference is manifest in the two-electron integrals in the molecular spinor basis that can be written, respectively, as real, complex, or quaternion numbers. We have currently completed the implementation of the complex (C_2, C_s, C_{2h}) and quaternion (C_i, C_1) groups. In the complex groups, integrals with an odd number of barred indices vanish and the active lists of integrals be-

come (in Mulliken notation): $(ij|kl)$, $(i\overline{j}|\overline{kl})$, $(\overline{ij}|\overline{kl})$, and $(i\overline{j}|k\overline{l})$. Integrals with four barred indices are also nonzero but related to the completely unbarred list via Kramers symmetry. This can be employed to remove reference to this class in the contraction loops.

In the quaternion groups the barred and unbarred spinors belong to the same fermion symmetry. If one does not employ quaternion algebra four additional integral lists appear. They are chosen as follows: $(i\bar{j}|kl)$, $(\overline{ij}|kl)$, $(\overline{ij}|\overline{kl})$, and $(i\bar{j}|\overline{kl})$. Again two of these classes are redundant since the classes with one bar are related to those with three bars. The corresponding excitation operators are, however, present explicitly in the computation of the sigma vector. We chose to exploit the redundancy by storing only the classes with one bar and creating the integrals with three bars ''on the fly'' when needed.

2. Integral storage

By analogy to our nonrelativistic formalism, integrals with 4 unbarred indices are stored as a Coulomb minus exchange integral, $(ij||kl)=[(ij|kl)-(il|kj)]$. In contrast to a nonrelativistic formalism, however, where one would either only need the Coulomb or the exchange part of the other types of two-particle integrals, we now find that both terms are always needed. Consider for instance the integral $(\overline{ij}|j\overline{i})$. Its nonrelativistic counterpart (unbarred indices corresponding to an α spin and barred to a β spin) vanishes upon spin-integration[34] but the relativistic integral is nonzero. To retain consistency in the nonrelativistic and the relativistic setup of the program we chose to store these types as separate integrals.

So far we have not considered the GAS partitioning of the active spinor space on which the wave function definition is based because it was not relevant for the preceding discussion. Since we now want to discuss the integral storage we need to pay attention to this aspect. The GAS partitioning gives rise to a substructure of integrals and density matrices that depends on the GAS classification of the involved indices. Figure 1 gives a pseudocode visualizing the procedure of fetching integrals and storing density matrices that follows this substructure. We chose to treat real and imaginary parts of all quantities separately and not to rely on the not always efficient complex algebra that compilers may offer. First we determine the type of excitation by the operator class (explained above) and the possible distributions of excitation operators over the active spaces. Next follows the number of electrons (varying from 0 to 2) for each of the in total four types (creation unbarred, creation barred, annihilation unbarred, annihilation barred) of individual creation/annihilation operators. Finally, we need three symmetry loops to itemize the possible symmetry combinations of the operator types that add up to the right overall operator symmetry (totally symmetric in case the operator is the Hamiltonian). Given this information, strings can be generated for each operator type. The final step is to loop over these strings, fetch the corresponding integrals, and store them in an internal list. This internal list can then be used in the sigma-vector or density-matrix construction. The full integral list is superfluous after this sorting step is completed and is released from memory when the fetching procedure is ended.

```
Real/imaginary part of integral
  Type of excitation
    Number of electrons per creation/annihilation of unbarred/barred
    Symmetry loop: total creation
      Determine total annihilation symmetry
      Symmetry loop: creation unbarred
        Determine creation barred symmetry
        Symmetry loop: annihilation unbarred
          Determine annihilation barred symmetry
          Get strings for creation/annihilation of U/B for no. of electrons
           and occupation
          String loop: annihilation barred
            String loop: annihilation unbarred
              String loop: creation barred
                String loop: creation unbarred
                  FETCH INTEGRAL FOR INDEX PAIR/QUADRUPLE
                  (and exchange integral if appropriate)
                end do
              end do
            end do
          end do
        end do
      end do
    end do
  end do
end do
```

FIG. 1. Loop structure for integral access in excitation class formalism.

The now generated internal integral list is string-driven and has a length which varies with the type of calculation that is specified. A unique ordering of all involved terms is defined automatically and this same ordering (and length!) can also be used to order the 1- and 2-particle density matrix elements that are computed after the CI calculation. The common set of routines for evaluating density matrices and sigma vectors will be discussed in the following subsection.

C. Sigma vector and density matrix routines

At the top level the generation of sigma vectors and density matrices in the new formalism proceeds in the same way as described in Ref. 10. In order to be able to compare with the ''traditional'' evaluation, the new scheme has been implemented as an alternative route. The most important aspects of the new implementation are summarized here.

Real and imaginary contributions to the vectors are treated separately by an outer loop over the different components. A partitioning of the vectors according to the Kramers projection values of the determinant elements is carried out and loops over the partitions are performed. At the innermost level, the occupation of the different GA spaces defines types of ''bra'' (in the following addressed as L, left) and ''ket'' (R, right) determinants. At this point, the decisive difference compared to the traditional route becomes clear. Whereas the conventional set-up would call distinct routines for all kinds of coupling types, differing, e.g., in the change in Kramers projection value ΔM_K and the number of electrons, the new setup calls the same routine for all couplings of the given L and R fragments no matter what form the coupling operator has. This concise implementation leads to a significant reduction of computer code.

As a further improvement, the evaluation of the coupling coefficients, e.g., in Eq. (4), is now carried out by introducing a resolution of the identity in the string basis $\mathbf{1}=\Sigma_{\mathcal{U}\overline{\mathcal{U}}}|\mathcal{U}^\dagger\overline{\mathcal{U}}^\dagger\rangle\langle\mathcal{U}^\dagger\overline{\mathcal{U}}^\dagger|$. In this resolution over all strings the unbarred and barred coupling coefficients may be treated separately,[17] as

$$A_{ijkl}^{\overline{\mathcal{TS}},\overline{\mathcal{SS}}}=\langle\mathcal{T}^\dagger|a_i^\dagger a_k^\dagger a_l|\mathcal{S}^\dagger\rangle\langle\overline{\mathcal{T}}^\dagger|a_j^\dagger|\overline{\mathcal{S}}^\dagger\rangle. \quad (5)$$

The procedure commences with loops over the different symmetry blocks of the resolution matrices and by grouping the strings according to the maximum allowed size of a single resolution batch. Because the determination of the coupling coefficients directly from the unbarred and barred string combinations becomes time-consuming in the limit of long CI expansions one gains a significant speed-up by introducing such resolution matrices. The price that is to be paid are increased operation counts, but these may be minimized by carefully considering the place where the resolution of the identity is inserted.

The final step in the sigma vector computation consists of multiplication of the R vector expansion coefficient by the integral value. For this, a full symmetry block of a particular excitation type of integrals is picked from the integral array and processed. In the density computation, the final contraction involves the L and R vector expansion coefficients and the appropriate summation over L strings. The generated order of density matrix elements exactly resembles the excitation class ordering of integrals described above. The code thus delivers general n-particle density matrices which will find their use in the relativistic MCSCF program.[18]

III. APPLICATIONS AND DISCUSSION

The current implementation opens for molecular applications on heavy element systems with pronounced spin–orbit effects in the one-particle basis, i.e., where a spin-dependent orbital optimization prior to the plain CI run is desirable. We want to demonstrate in a few test cases the improvement of the new implementation over the previous one where a spin-averaged basis of one-particle functions is the starting point.

A. Heavy atoms

We start with a study on atoms that have either one electron outside or one hole in a closed shell core as this provides the simple example of spin–orbit splitting in the ground state. We thereby consider p-, d-, and f-shells as the influence of orbital relaxation should be rather different in either case. To obtain the best comparison we select atoms of sizable and similar nuclear charge. Our systems of choice are thallium (Tl,$6s^2p^1$,$^2P_{1/2,3/2}$), lutetium (Lu,$5d^16s^2$,$^2D_{3/2,5/2}$), and thulium (Tm,$4f^{13}6s^2$,$^2F_{7/2,5/2}$), the configuration and level symbol of the ground state given in parentheses.

The MOLCAS program package (version 5.0[9]) served to find a scalar relativistic, spin-averaged orbital basis for the three atoms whereas DIRAC was used for the spin–orbit relaxed calculations. To enable a fair comparison we used an uncontracted basis set in both cases. A set of family type is used for the Tm and Lu atoms[19] with $23s$, $19p$, $17d$, and $11f$ exponents. The Tl basis set consisted of $20s$, $16p$, $11d$, and $8f$ functions. Spin–orbit mean-field integrals were generated with the atomic mean-field integrals(AMFI)[20] program. Here we encountered a technical complication because the MOLCAS-AMFI implementation defines its mean-field based upon the atomic contraction coefficients of the basis functions. In an uncontracted calculation this would mean that the core spinors were to be represented by single GTOs, which is too crude an approximation to be used. In this case we used a modified version of AMFI, that includes a call to an initial SCF module to calculate atomic orbital coefficients for computing the appropriate mean-field integrals.

The symmetry group used is C_{2h}^* in the spin-averaged and C_2^* in the DIRAC calculations, giving rise to 3 roots for Tl (A_u,A_1), 5 for Lu (A_g,A_1), and 7 for Tm (A_u,A_1), respectively. To avoid spurious symmetry-breaking in the spin-averaged calculations, orbitals are symmetrized by optimizing on multiple roots in a complete active space self-consistent field (CASSCF) calculation using the Tl^+, Lu^+, and Tm^- SCF orbitals as a starting point. In the spinor-type calculations symmetry-breaking does not occur as DIRAC by default optimizes on a state-averaged energy expression using fractional occupation of the open shell orbitals. We then build the corresponding one-determinant wave functions as a zeroth-order approximation, and perform different kinds of variational (spin–orbit) CI calculations:

(1) CAS type CI: Full CI within the valence subspace, giving the spin–orbit splitting of the respective ground states.
   (a) Minimal CAS: Only the open sub-shell angular momentum functions are included: $4f^{13}$ in Tm, $5d^1$ in Lu, and $6p^1$ in Tl. This excludes any correlation contribution.
   (b) Valence CAS: In Lu the active space becomes $6s^25d^1$, in Tl $6s^26p^1$, and in Tm the valence CAS space is identical to the minimal CAS. This has the effect of including a minimal amount of correlation between the valence electrons and gives rise to a modification of the spin–orbit splitting of the ground state.

(2) SD(T) type CI: including all single, double, (and triple) replacements from the minimal CAS reference occupation into a restricted virtual space. This restriction is to be imposed in uncontracted basis set calculations since numerous high energy virtuals appear. A cut-off threshold of 10 a.u. (3 a.u. for Lu) for the orbital energy prevents inclusion of high-lying virtual orbitals that contribute little to electron correlation and would make the virtual space prohibitively large. In the cases of Tm and Lu, there are too many triple replacements to allow for SDT-CI calculations when correlating 15 or 17 electrons, respectively. For Tl this was feasible so that we include triple excitations as well in that case.

The DIRAC calculations with the newly developed CI code (described here) use the same setup as the spin-averaged MOLCAS calculations: An uncontracted basis set and deletion of virtual spinors with energies above 10 a.u. (3 a.u). The resulting CI expansion lengths are $\approx$70.000 terms

TABLE II. Ground-state spin–orbit splittings in cm^{-1} and differences in radial expectation values of the valence spinors in a.u.

Atom	Tm		Lu		Tl	
Valence spinors	$f_{7/2}-f_{5/2}$		$d_{3/2}-d_{5/2}$		$p_{1/2}-p_{3/2}$	
$\Delta\langle r\rangle$	0.018		0.085		0.496	
Approach	Orbitals	Spinors	Orbitals	Spinors	Orbitals	Spinors
Minimal CAS	9108	8996	2578	1687	6330	7709
Valence CAS	···	···	2470	1564	6260	7083
SD(T)CI	9817	9280	2450	1744	7200	7286
Exp.	8771.243[a]		1993.32[b]		7793[c]	

[a]Reference 31.
[b]Reference 31.
[c]Reference 32.

in the SDT calculations on Tl and ≈1.1 million determinants in the SD calculation on Tm including 15 electrons.

The results of these calculations are summarized in Table II. The first observation is the striking difference between the minimal CAS and the valence CAS spin–orbit splitting in Thallium in the spinor calculation. It turns out that this phenomenon can be explained via second-order perturbation theory. The valence CAS space of Tl gives rise to the configurations s^2p^1, s^1p^2, and p^3. The first configuration is also present in the minimal CAS space and gives the zeroth-order (one-determinant) description of the ground-state wave function. In the valence CAS also states from p^3 can mix in. The ground-state component $^2P_{1/2}$ interacts with one excited determinant whereas the $^2P_{3/2}$ component interacts with two determinants. The coupling matrix elements are

$$\langle s\bar{s}p_{1/2}|\hat{H}|p_{1/2}p_{3/2}\bar{p}_{3/2}\rangle$$
$$=\langle s\bar{s}p_{3/2}|\hat{H}|p_{3/2}p_{3/2}\bar{p}_{3/2}\rangle\approx -0.048E_H$$
$$\langle s\bar{s}p_{3/2}|\hat{H}|p_{1/2}\bar{p}_{1/2}p_{3/2}\rangle\approx 0.060E_H.$$

These matrix elements differ in value due to the fact that the $p_{1/2}$ spinor is more compact than the $p_{3/2}$ spinor which makes the integral $\langle s\bar{s}|1/r_{12}|p_{1/2}\bar{p}_{1/2}\rangle$ larger than $\langle s\bar{s}|1/r_{12}|p_{3/2}\bar{p}_{3/2}\rangle$. Taking also the difference in diagonal elements into account and using the second-order perturbation theory expression:

$$E_J^{(2)}=\sum_n \frac{|\langle {}^2P_J(s^2p^1)|\hat{H}|{}^2P_J^n(p^3)\rangle|^2}{\Delta E_J}, \quad J=1/2,3/2,$$

n labeling the different state components and ΔE_J denoting the energy difference between the diagonal elements in the determinant basis we find the following energy lowerings:

$$E_{1/2}^{(2)}=-1760.4\ \text{cm}^{-1},$$
$$E_{3/2}^{(2)}=-2604.5\ \text{cm}^{-1},$$

the difference amounting to 844 cm^{-1}. The variational treatment in the true complete active space configuration interaction (CASCI) gives a difference of 626 cm^{-1} in the same direction. This demonstrates that limited or unbalanced introduction of electron correlation effects may worsen the results of the calculation instead of improving them.

As we wanted to focus on a rigorous comparison between the orbital and spinor approach and not on obtaining spin–orbit splittings of very high precision we did not attempt to fully converge the computed splitting. This requires among others including the $5d$ for correlation in the thallium atom.[10] Running this type of calculation with the spinor basis and a truncation value of 2 a.u. for the virtual spinors results in a splitting of 7420 cm^{-1} (21 virtual Kramers pairs, 1.288.980 determinants). This value can further be improved by increasing the size of the virtual space and by including also the outer core $5p$ shell in the correlation treatment.[35] Whereas this method provides for systematic improvement in case of spinor calculations this is not so for orbital calculations. There one may obtain virtually any desired splitting by an unbalanced correlation treatment. Then one finds that, e.g., including all virtual functions when correlating only 3 valence electrons brings the ground-state splitting to twice its experimental value, because the improvement of the valence function is not accompanied by simultaneous improvement of the core functions to which this function needs to be orthogonal (see the discussion in Ref. 21). We confirmed this finding also with the Douglas–Kroll Hamiltonian by increasing the cutoff threshold in several steps, yielding an increasing spin–orbit (SO) splitting beyond the experimental value. Thus, to maintain a balanced description of the spin–orbit components, the extent of the virtual space should be kept in accordance with the electrons chosen to be correlated. Full convergence of the atomic SO-splitting of Tl requires long expansions, which are feasible using dedicated programs that employ spherical symmetry.[22]

Turning to the other atoms we see that, as expected, the small difference in radial expectation values between the f spinors in Tm do not cause a big difference in the determined spin–orbit splittings in the orbital or spinor approach at the valence CAS or SDCI level. The spinor basis performs better but in both cases the minimal CAS result is acceptable. Lu comprises an intermediate case: The difference in radial expectation values is about a factor of 5 larger than in Tm, but is still smaller by about the same factor than the Tl splitting.

The valence CAS calculation for Lu exhibits a similar unbalanced treatment of the component correlation as in Tl, but here the effect is noticeably smaller. Correlating also the $4f$ electrons leads to a significant improvement of the spin–

TABLE III. ClO ground-state spin–orbit splittings in cm^{-1} at different correlation levels and using different approaches.

Approach	Orbitals[a]	Orbitals+G	sf+so	Spinors	Spinors+G[b]
(9in5)CAS	224.3	206.9	221.8	245.1	
(9in6)CAS	228.9	211.5	226.3	250.9	
(13in8)CAS	229.6	212.2	227.0	252.1	
SD9-3au	291.9	274.3	289.5	313.1	est. 293
Reference				244.8	225.9
CCSD				324.4	303.5
CCSD-T				336.4	315.3
Exp[c]			318		

[a]Computed with a modified version of the AMFI code including only the one-electron and the two-electron spin–same–orbit terms (Ref. 20).
[b]Reference 24.
[c]Reference 33.

orbit splitting in the spinor basis whereas the orbital value hardly changes. By applying the sf+so approach (described in the section on ClO) and correlating also the $5s$ and $5p$ semicore (25 electrons in total), we obtain a value of 2031 cm^{-1} in the orbital basis which is quite close to experiment.

In all cases the spinor basis gives reasonable results for the minimal CAS space, and significant improvement can only be reached by going to rather large expansions. This is of particular interest when multiconfiguration SCF type of calculations are carried out where a limited active space is mandatory. Given this future development and the fact that spin-dependent type of CI calculations will become prohibitively expensive anyhow when the system size and the number of virtual functions is increased, we consider the present limited size calculations rather typical. They may be very useful[23] in complicated situations where a good choice of reference function is difficult and application of coupled-cluster methods is impossible.

B. A molecular example: ClO

In order to compare with other methods[24,25] we chose to investigate the molecule ClO that represents a light molecule with a significant spin–orbit splitting lifting the degeneracy of the ground state. In earlier work it was demonstrated that a correlation treatment is indispensable for achieving a ground-state spin–orbit splitting of even acceptable accuracy. The obvious reason is the poor description of the electron affinities of the constituent atoms at the SCF level of theory. It will be interesting to see whether CI calculations will give the same trends. Thus, we have carried out a series of calculations in both the orbital and the spinor basis at different correlation levels. The results are compiled in Table III.

The types of calculations in the table are denoted as follows: CAS stands for a full CI calculation in the aforementioned subspace, e.g., (9in5)CAS characterizes a calculation with nine active electrons in five Kramers pairs, which in this case simply is the valence orbitals/spinors $\sigma_p, 2\pi_p, 2\pi_p^*$ constructed from the p orbitals/spinors. The sixth function is the σ_p^* orbital, and the two additional orbitals in the (13in8) calculation refer to the σ_s and σ_s^* occupied orbitals. Furthermore, CI singles and doubles (SD) calculations have been carried out with nine and 13 electrons, respectively, limiting the virtual space to orbitals/spinors with energies below 3 a.u.. We compare the results both with experiment and the previous values obtained with the Dirac–Coulomb–Gaunt Hamiltonian and one set of spinors (DCG1) at the SCF level (reference) and the Coupled Cluster method with single, double and perturbative inclusion of triple excitations. We took the same basis set as in Ref. 24 but used it in uncontracted form. This difference is only 0.3 cm^{-1} as can be seen by comparing the CCSD one-determinant reference value with the (9in5)CAS value (both numbers should be identical if the same basis is used). The neglect of the Gaunt interaction is important as is apparent by looking at the fourth and fifth column of Table III where we list the Dirac–Coulomb and Dirac–Coulomb–Gaunt results computed with the MOLFDIR program.[26,27] The effect of the Gaunt interaction is an almost constant shift of 20 cm^{-1} that reduces the computed splitting. The spin–other–orbit contribution to the splitting increases slightly with the correlation treatment, and we give an estimated (final) value for the SD9 CI calculation including the estimated Gaunt contribution at this level of correlation from the MOLFDIR CC calculations.

The CISD approach that we used in the present work gives a splitting that is 10 cm^{-1} smaller than the CCSD value and falls about 23 cm^{-1} short of the benchmark CCSD-T value. This illustrates the well-known shortcomings of the CI method to assess the full correlation energy. More important in the present context is, however, that we again find that the spinor basis performs significantly better than the orbital basis, even for such a light molecule as ClO. However, another issue needs attention when doing such a direct comparison: The orbital values in the first two columns of Table III have been obtained including two further approximations. First, a mean-field spin–orbit summation is carried out, and, furthermore, spin–orbit integrals are computed neglecting multicenter terms (the atomic approximation). To further resolve this and refine the comparison, we also report results of a hybrid approach in the third column (denoted sf+so). These are obtained by first generating a molecular orbital basis using the spin-free DIRAC formalism.[16] Next, the implementation of the integral transformation step in DIRAC allows for transforming spin-dependent integrals [using the Dirac–Coulomb (DC) operator] to this spin-free orbital basis, but without invoking a mean-field summation and also including two-center spin-dependent integrals. Thus, the combined contribution of the mean-field summation and the one-center approximation in AMFI can be ruled out. In fact, as can be seen by comparing these results with the orbital values, the latter effects are negligibly small, amounting to only 2 to 3 cm^{-1}, which is also a corroboration of the validity of the AMFI approximations. What remains is a difference of roughly 25 cm^{-1}, which is solely due to the methodological treatment of spin–orbit coupling: Early (at the SCF stage) or late (at the CI stage). The present results indicate a surprisingly large superiority of the spin-dependent orbital optimization already for elements as light as chlorine and oxygen.

IV. CONCLUSIONS

On the technical side we report that the LUCIAREL program has now been included in, and adapted to, a program-package which uses a general relativistic spinor basis. Thus, it is now possible to exploit the advantages of the GAS approach in a spinor basis when, e.g., heavy element compounds are investigated. Moreover, the concise program code for determining sigma vectors and density matrices improves transparency and facilitates future modifications and improvements. The only point of reference of this CI program is the Kramers pairing of the optimized spinors, and it is not decisive whether a ''full'' Dirac Hamiltonian or an approximate spin-dependent Hamiltonian which typically is two-component is used to determine the spinor basis. The former option will leave the electronic and positronic degrees of freedom open for optimization in the Hartree–Fock procedure (and thus requires both large and small component basis functions). In this context LUCIAREL will serve as the large-scale CI module for a new Kramers-MCSCF program within the DIRAC package.[18,28] The composite treatment of sigma vectors and density matrices proves valuable for the implementation of this module.

Use of a spinor basis has a profound impact on the efficiency of determining atomic spin–orbit splittings, both in uncorrelated and correlated treatments. We conclude at this stage that the well-known test case Tl does not stand alone in this respect, but that also the lanthanide atomic ground states under consideration are better described in a spinor basis at a given level of electron correlation. Our study is meant to exemplify the difference in these representative cases, and there is all reason to assume that the finding will carry over to molecules with heavy atoms, including those different from the ones we have selected.

In conclusion, we recommend to start from a spinor basis when an extensive correlation treatment is aimed at. Since the presented CI calculations are equally expensive for Dirac spinors as for approximate spinors derived from an approximate spin-dependent Hamiltonian (like the Douglas–Kroll Hamiltonian including the Breit interaction), there would in principle be no argument for applying an approximated Hamiltonian once the correlation stage begins to dominate the calculation time. Two counter arguments should be mentioned, however. At the present stage of implementation, the use of uncontracted basis sets in the 4-component approach is less efficient than the use of general contraction as is common in correlation calculations with a scalar relativistic Hamiltonian. This is especially important when a number of heavy atoms are to be taken into account. Second, the AMFI method also takes the Breit interaction into account in an approximate fashion, whereas our Dirac calculations employ the Dirac–Coulomb operator which neglects the spin–other–orbit terms of the relativistic two-particle interaction. Although these contributions are relatively small in heavy elements, it would be desirable to include them. This will be subject of future work on the DIRAC package.[29] We also like to mention here that an implementation of the mean-field spin–orbit method based upon molecular densities within the DIRAC package is in progress.[30]

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[34] In other words, since there is no exchange interaction between particles with different spin.

[35] It has to be noted, though, that taking the spin–other–orbit part of the two-electron spin–orbit operator into account would result in a decrease of the spin–orbit splitting of Tl in the order of $50\ \mathrm{cm}^{-1}$ (Ref. 2) in our present spinor calculations. In the orbital calculations, the Gaunt term is accounted for in an approximate fashion through the mean-field summation.